EXHIBIT A

The Electrochemistry of Diamond

by

Matthew Neil Latto
University of Bristol
School of Chemistry
Faculty of Science

A dissertation submitted to the University of Bristol in accordance with the requirements of the degree of
Doctor of Philosophy in the Faculty of Science

September 2001

CONTENTS

word count (chapters 1 - 9): 29,227
word count (all text): 38,805

Table of Contents

Chapter 4
Standard Electrochemical Theory

4.0 Outline

- This chapter outlines the standard electrochemical theory on which this study was based.
- A comparison is made between the behaviour of metal and semiconductor electrodes.
- An expression is derived relating the steady state current to the overpotential for surface state mediated charge transfer.

4.1 Metal Electrochemistry

In this section the Marcus-Gerischer theory for electron transfer at a metal electrode is outlined. Reference 119(a) contains details of the theory and lists the original references and review articles. Underlying this approach is the idea that electron transfer occurs between occupied and unoccupied states that are equal in energy. [120]

The total current density, j, at a metal-solution interface is the sum of the anodic current density, j_a, and the cathodic density, j_c. By convention, the cathodic current is negative.

$$j = j_a + j_c . \qquad \text{(equation 4.1)}$$

Anodic current flows when oxidation occurs at the electrode surface:

$$R \rightarrow O + e^- \qquad (\text{e.g. } Fe^{2+}_{(aq)} \rightarrow Fe^{3+}_{(aq)} + e^-)$$

Cathodic current flows when reduction occurs at the electrode surface:

$$O + e^- \rightarrow R \qquad (\text{e.g. } Fe^{3+}_{(aq)} + e^- \rightarrow Fe^{2+}_{(aq)})$$

In the Marcus-Gerischer approach to electron transfer it is assumed that the Born-Oppenheimer approximation applies, i.e., the nuclei, being so much heavier than the electron, move relatively slowly and may be treated as stationary during electron transfer. [121] Hence electrons are transferred to energy levels at or near the Fermi level in the metal. At a metal electrode a change in the applied potential results in charging of the metal which leads to a change in the potential at the surface. As the energy of the surface electrons is altered the position of the Fermi level changes. However, the occupation of states about the Fermi level remains constant. As a result the current densities are simply proportional to the overlap integral of the Fermi function in the metal and the density of states function for the solution species:

$$j_a \propto (\text{overlap of } E_F \text{ and } E_R)$$

$$j_c \propto - (\text{overlap of } E_F \text{ and } E_O)$$

Figure 4.2 shows a schematic energy diagram for a metal-solution interface.

At the equilibrium potential, the overlap integrals are equal. The values of j_a and j_c are therefore equal and opposite and the net current density is zero. This situation is shown to the left in figure 4.2.

At a positive overpotential, the overlap integral for the reduced species is greater than that for the oxidised species. The net current density is therefore positive. An anodic current flows and oxidation of the reduced species occurs. This situation is shown in the upper right diagram in figure 4.2.

At a negative overpotential, the overlap integral for the oxidised species is greater than that for the reduced species. The net current density is therefore negative. A cathodic current flows and reduction of the oxidised species occurs. This situation is shown in the lower right diagram in figure 4.2.

Figure 4.1 shows a sketch of current density – overpotential relationship for the case where the transfer coefficient, $\alpha = ½$.

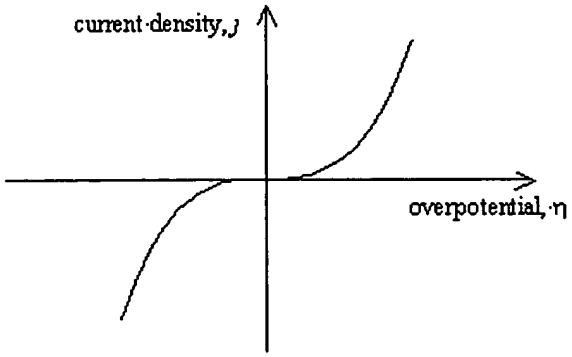

Figure 4.1 – current density as a function of overpotential for a metal

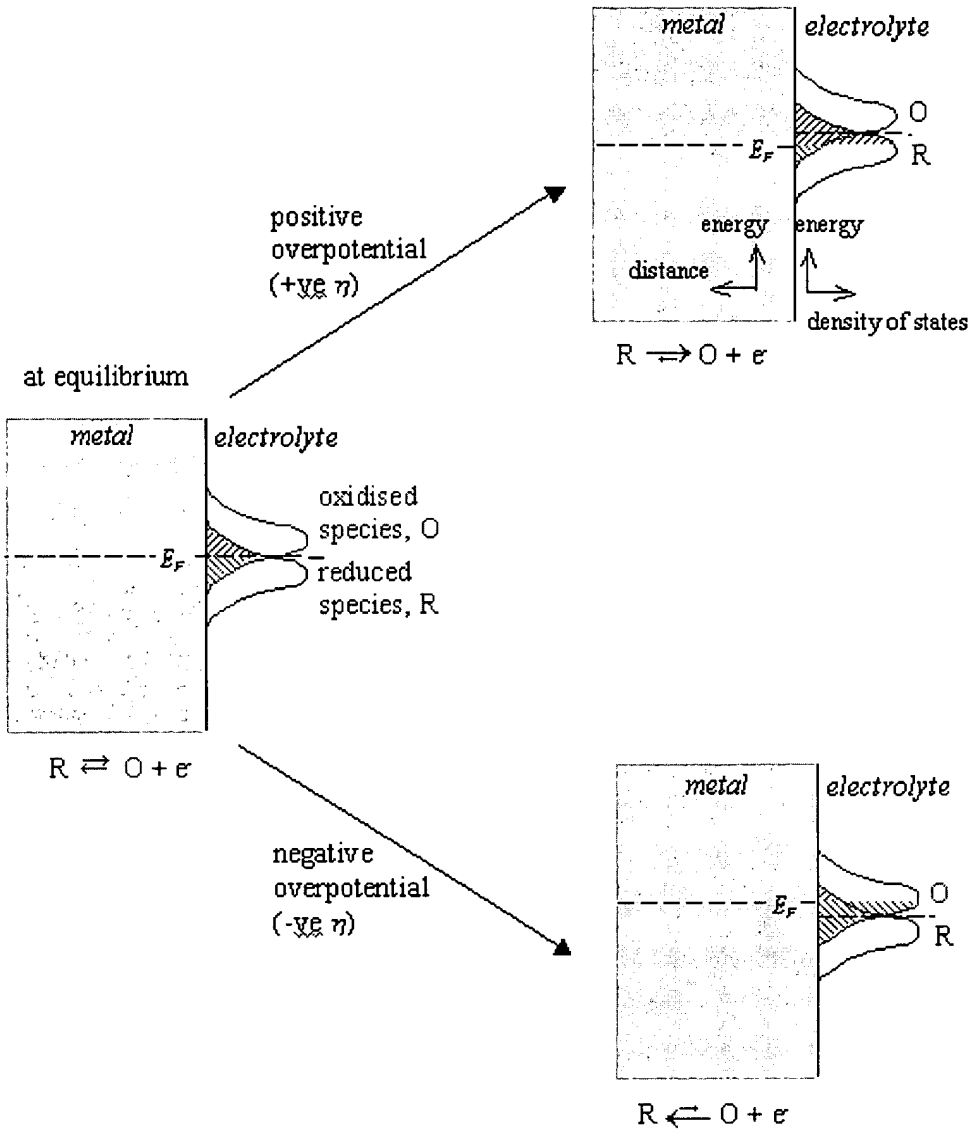

Figure 4.2 – Schematic Energy Diagram for a Metal-Solution Interface

4.2 Normal p-type Semiconductor Electrochemistry

As for a metal electrode, the total current density, j, is the sum of the anodic and cathodic current densities (j_a & j_c). The majority charge carriers in a p-type semiconductor are positive holes in the valence band.

The anodic reaction:

$$R + h^+_{(VB)} \rightarrow O \qquad (e.g.\ Fe^{2+}_{(aq)} + h^+_{(VB)} \rightarrow Fe^{3+}_{(aq)})$$

The cathodic reaction:

$$O \rightarrow R + h^+_{(VB)} \qquad (e.g.\ Fe^{3+}_{(aq)} \rightarrow Fe^{2+}_{(aq)} + h^+_{(VB)})$$

The Born-Oppenheimer approximation still applies but unlike the case for a metal electrode, charge transfer can not occur at the Fermi level if the density of states is zero at that energy (i.e. it is in the band gap of the semiconductor). Charge transfer will occur at the surface energy of the valence band, $E_{VB,S}$.

Current flow at a semiconductor electrode is dependent of the surface concentration of majority charge carriers. For a p-type semiconductor, the concentration of holes at surface is a significant factor in the rate of charge flow in the anodic reaction:

$$j_a \propto \text{(overlap of } E_{VB,S} \text{ and } E_R) \times ([h^+]_{surface})$$

Whilst for the cathodic reaction the availability of electrons in the valence band is essentially constant:

$$j_c \propto -\text{(overlap of } E_{VB,S} \text{ and } E_O)$$

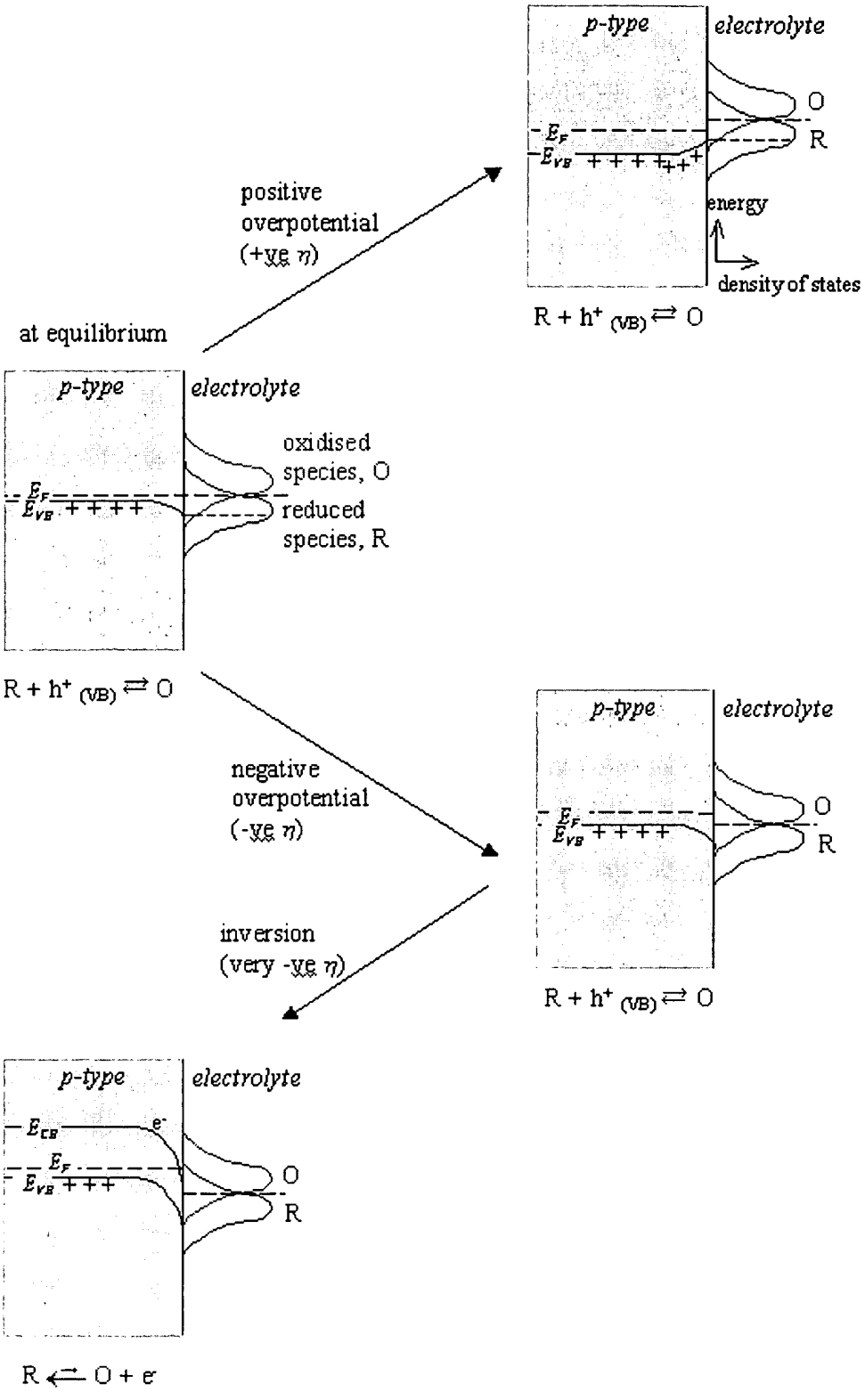

Figure 4.3 – Schematic Energy Diagram for a Semiconductor-Solution Interface

The overlap terms at the valence band edge are not affected by changes in potential. The cathodic current density will therefore remain constant.

$$j_c = j_{c,0}$$

At a positive overpotential, there will be a higher surface concentration of holes than at equilibrium. There is an exponential relationship between the concentration of holes and the overpotential. Therefore, at positive overpotential, the anodic current density will be greater than at equilibrium.

$$j_a > j_{a,0}$$

At negative overpotential, the concentration of holes at the surface will be reduced and as the magnitude of the negative overpotential is increased, the concentration will tend to zero. The anodic current density, j_a, will therefore fall from its equilibrium value, $j_{a,0}$.

The total current density, j, is the sum of the constant cathodic current density, j_c, and the variable anodic current density, j_a. At increasing positive overpotential, the total current density will rise rapidly, while at decreasing negative overpotential, the total current density will fall to a constant minimum value, equal to the equilibrium cathodic current density, $j_{c,0}$.

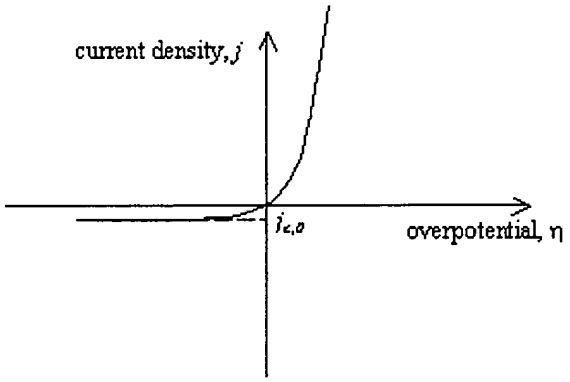

Figure 4.4 – current density as a function of overpotential for a semiconductor

At sufficiently negative potentials, inversion can occur. This phenomenon occurs when band bending at the surface of the semiconductor is sufficiently great that the Fermi level lies in the conduction band. There will then be a finite probability of finding a conduction band electron at the surface of the semiconductor. An anodic current can flow and the total current density will be reduced in magnitude ($j_{c,0} < j < 0$).

Anodic current flow due to inversion:

$$O + e^-_{(CB)} \rightarrow R \qquad (\text{e.g. } Fe^{3+}_{(aq)} + e^- \rightarrow Fe^{2+}_{(aq)})$$

4.3 Highly doped semiconductors

At high doping levels, the semiconductor becomes *degenerately* doped. The Fermi Level of the semiconductor lies within the valence band (VB) and the space charge region becomes very small. Electrons are able to tunnel from the bulk VB directly into the electrolyte. Therefore, the concentration of available charge carriers is constant and the electrode behaves like a metal.

$$j_a \propto (\text{overlap of } E_F \text{ and } E_R)$$

$$j_c \propto - (\text{overlap of } E_F \text{ and } E_O)$$

Cyclic voltammograms will therefore show both oxidation and reduction peaks.

Figure 4.5 shows a schematic energy diagram for a highly doped semiconductor-solution interface.

Figure 4.6 shows a sketch of current density – overpotential relationship.

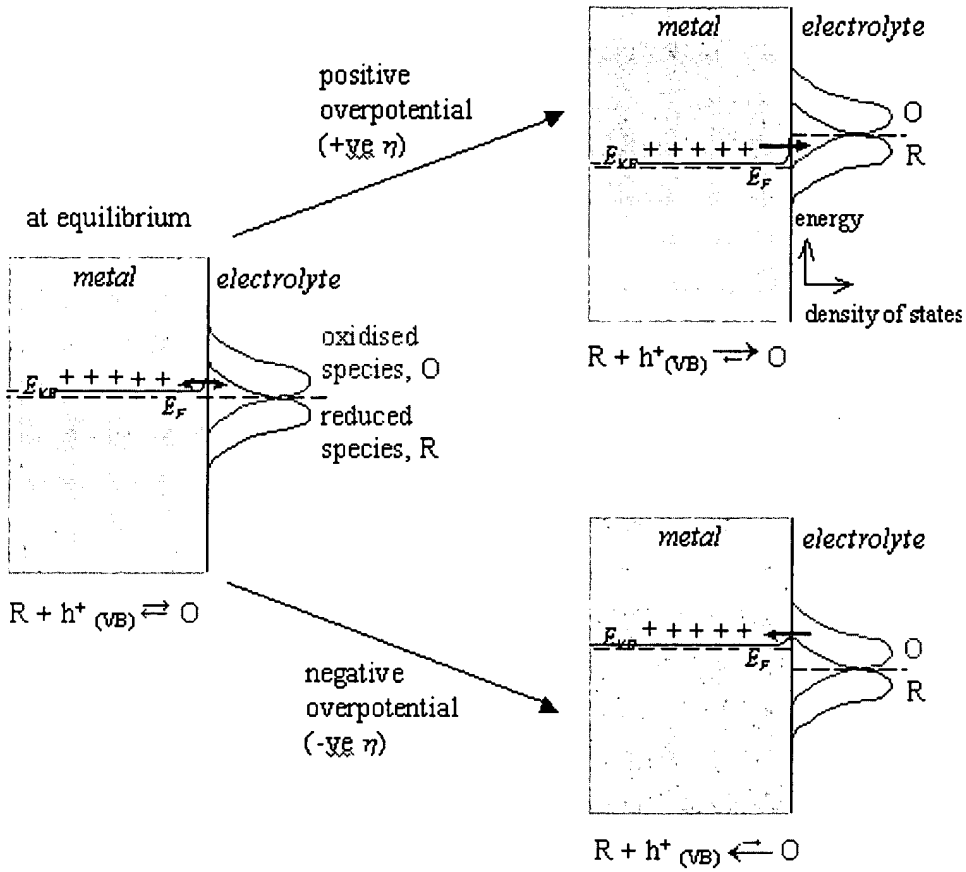

Figure 4.5 – Schematic Energy Diagram for a Heavily Doped Semiconductor-Solution Interface

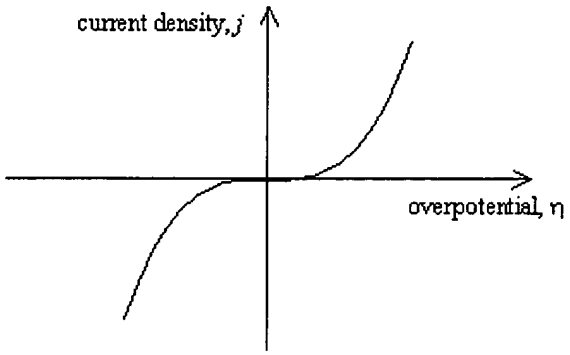

Figure 4.6 – current density as a function of overpotential for a heavily doped semiconductor